

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
27 January 2005 (27.01.2005)

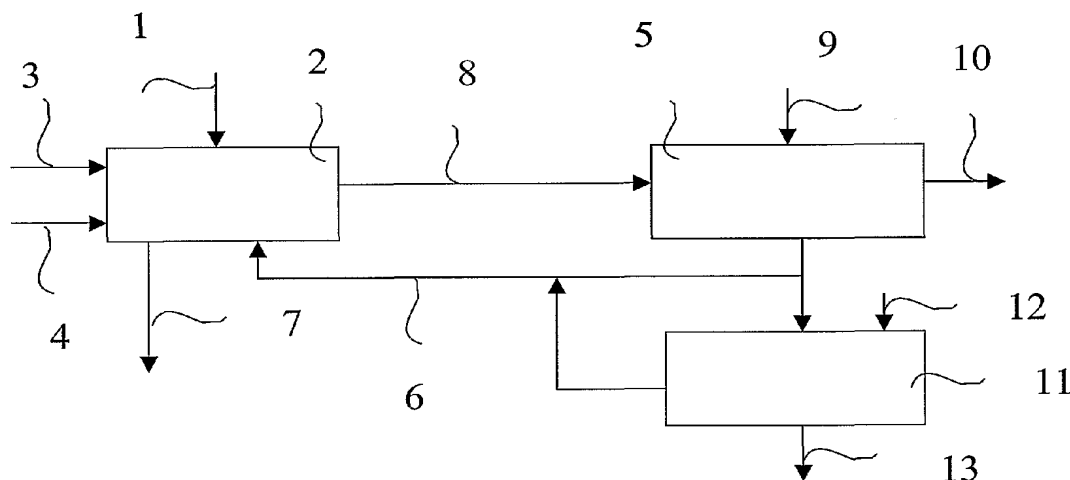
PCT

(10) International Publication Number
WO 2005/007901 A1

- (51) International Patent Classification⁷: **C22B 3/06** // 15:00
- (21) International Application Number: **PCT/FI2004/000452**
- (22) International Filing Date: **14 July 2004 (14.07.2004)**
- (25) Filing Language: **Finnish**
- (26) Publication Language: **English**
- (30) Priority Data:
20031084 **17 July 2003 (17.07.2003)** **FI**
- (71) Applicant (for all designated States except US): **OUTOKUMPU OYJ** [FI/FI]; Riihitontuntie 7, FIN-02200 Espoo (FI).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): **HEIMALA, Seppo** [FI/FI]; Marjastajantie 9, FIN-28220 Pori (FI). **RUONALA, Mikko** [FI/FI]; Lumimarjantie 16, FIN-28220 Pori (FI).
- (74) Agent: **OUTOKUMPU OYJ, INTELLECTUAL PROPERTY MANAGEMENT**; P.O. Box 27, FIN-02201 Espoo (FI).
- (81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

[Continued on next page]

(54) Title: METHOD FOR PROCESSING SULFIDE ORES CONTAINING PRECIOUS METALS



(57) Abstract: The invention relates to a method for processing sulfide ores containing precious metals, such as copper ores containing nickel. According to the method, the ore or concentrate (1) containing the precious metals is leached (2), and the iron contained in the solution is neutralized in oxidizing conditions by means of a ferrous recirculation solution (6) recirculated to the leach. The solution (8) from the leaching step and at least part of the solution residue is conducted to a conversion step (5), where iron bearing sulfide (9) is fed for turning the copper contained in the conversion step to copper sulfide concentrate (10) containing the precious metals. The solution (6) obtained from the conversion step is partly recirculated to the preceding leaching step (2) and partly conducted to the further treatment (11) of the components contained in the solution.

**Declarations under Rule 4.17:**

- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii)) for the following designations AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW, ARIPO patent (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE,

IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG)

- of inventorship (Rule 4.17(iv)) for US only

Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

METHOD FOR PROCESSING SULFIDE ORES CONTAINING PRECIOUS METALS

The present invention relates to a method for processing sulfide ores containing
5 precious metals, such as copper ores containing nickel.

At present nickel bearing copper ores are processed by flotation, so that there are directly and selectively produced separate copper and nickel concentrates, or then nickel concentrate is produced by depressing from a combined copper-
10 nickel concentrate. The precious metals, such as gold, platinum and palladium contained in the raw materials are later separated in the further processes of copper and nickel. Almost without exception, copper-nickel separations include known sub-steps that reduce recovery and increase expenses, such as the repeating of the copper concentrate for increasing copper content and for
15 lowering nickel content. Often precious metals are conducted from combined concentrates directly, in connection with smelting, to copper or nickel matte, especially if the copper and nickel quantities are relatively small with respect to the precious metals.

20 A few processes, different from those mentioned above, are being developed. The most typical of these is the process developed by Lakefield, based on the combined use of sulfuric acid (H_2SO_4) and hydrochloric acid (HCl) and autoclave conditions for leaching platinum-palladium-gold-copper and nickel bearing concentrates directly, so that all valuable components should go to the
25 solution. The temperature employed in the process is $210 - 230^\circ \text{C}$. Said conditions mean that for example all sulfidic sulfur is oxidized into sulfate. The commercial application of this process type is restrained for example by the high oxidation potential needed in the leaching of precious metals, the sometimes strong tendency of said minerals to be passivated, their tendency to
30 be adsorbed in refuse minerals in solution-solids separations, their tendency to remain in precipitations in connection with leaching, and to be cemented due to the effect of the remaining non-sulfatic or corresponding sulfur compounds.

When also the raw material, i.e. platinum-palladium-copper-nickel concentrate, is often poor, and the temperature range of over 200° C is economically expensive, the total leaching process becomes impractical for the above mentioned raw materials.

5

A third known process type is represented by the chloride assisted hydrometallurgical method described in the US-patent 5,902,474. Although the method, i.e. a process system utilizing mainly two-step leaching (autoclave + atmospheric) and liquid-liquid extraction, is meant for the recovery of copper
10 and zinc, it also takes into account, in a restricted way, some requirements set by precious metals.

The object of the method according to the invention is to alleviate drawbacks of said known processes of ores containing precious metals, such as copper ores
15 containing nickel, connected both to the copper-nickel separation and to iron(copper + nickel) separations, but particularly to the recovery of precious metals, such as platinum, palladium and gold, as well as to alleviate the drawbacks connected to the process expenses. The method utilizes, in the various process steps starting from concentration, the principles described for
20 example in the patents US 5,108,495 and US 4,561,970, for controlling the processes in terms of the conditions set by the minerals, so that the leaching step or the conversion step are at least partly controlled by means of mineral-specific potentials, impedance values or content values. As such, the method does not even attempt at leaching precious metals. In case precious metals are
25 obtained in the solution, they are cemented in the sediment for example by means of sulfides at the end of the leaching. The essential features of the invention are enlisted in the appended claims.

In a method according to the invention, at least part of the ore containing
30 precious metals, and possibly some other material containing valuable components (nickel, cobalt, copper) is advantageously leached in sulfate or chloride based leaching, or in a leaching based on a combination of these, as

atmospheric leaching in the temperature range of 50 – 105° C. The leaching can also be carried out in an autoclave. As a result from the leaching, there is obtained a solution containing iron, copper, nickel and cobalt, as well as possibly part of the precious metals, and a leaching residue. Copper sulfide and
5 the precious metals contained by copper sulfide may remain partly undissolved. The solution, and at least part of the leaching residue, is conducted to at least one conversion step, i.e. to sulfidizing cementation. In the conversion, the copper and possible precious metals contained by the solution are cemented by an iron bearing sulfide, advantageously by a $\text{CuFeS}_2\text{-(Ni,Fe,Co)}_9\text{S}_8(\text{Fe}_{1-x}\text{S})$
10 concentrate containing as large a share of the precious metals as possible and different sulfides in the temperature range 90 – 200° C, preferably in the temperature range 150 – 190° C, when necessary according to the principles defined in the patents US 5,108,495 and US 4,561,970, as electrochemically adjusted. The sulfide material used in the conversion can be the same material
15 or different material than the material going to leaching.

As a result from the conversion, there is obtained a copper-rich Cu_xS concentrate and a solution containing nickel, cobalt and iron. This solution, in which there can, when desired, also be added part of the leaching residue from
20 the leaching step, is conducted to nickel and cobalt recovery, for example to the production of nickel, or it is precipitated, at least in one conversion step, by means of iron sulfides, such as Fe_{1-x}S or FeS , into nickel sulfide or cobalt sulfide or a combination of these. The iron is removed as jarosite precipitate or oxide precipitate. The method also gives a possibility to an effective treatment
25 of nickel and cobalt bearing pyrrhotite, Fe_{1-x}S . The copper-rich Cu_xS concentrate containing the precious metals is further conducted to copper production, in connection with which the precious metals are recovered.

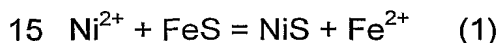
According to the method, the processing of mixed copper-nickel raw materials
30 is advantageously controlled. This is due to the fact that in the method, the copper and nickel recoveries are remarkably increased, when it is not necessary to separate the nickel by depressing from the copper concentrate, if

the concentration step is required before the leaching step. A similar advantage is also connected to iron sulfides, especially to pyrrhotite (Fe_{1-x}S). Owing to other precipitation phases and impurities contained by pyrrhotite, the recoveries of iron sulfide ores, for example with respect to copper, platinum and palladium, are radically reduced, if pyrrhotite is depressed for example in flotation, as is the case in the conventional process chain. When necessary, the taking of all pyrrhotite along in the leaching does result in a lot of iron oxide precipitate and elemental sulfur as a product from the leaching. Iron oxide precipitate and elemental sulfur can be processed into a harmless form as such by using various known methods including different steps.

According to the invention, for the material to be treated it suffices that advantageously only silicates are separated from the valuable components in the concentration. Still it is generally appropriate to create the gravitation concentrate as separate, because in the grinding, part of the minerals in the platinum-palladium group remains coarse, and flotation recoveries are low for these heavy and coarse minerals. At least the iron sulfide Fe_{1-x}S that is richest in nickel and cobalt is taken along in the combined concentrate to be treated.

An advantage of the method according to the invention, in comparison with the conventional copper smelting process, is for example that a high nickel content in the copper concentrate can be technically controlled at the same time as the precious metals are advantageously recovered along with the copper concentrate. As a product from the method according to the invention, there is obtained a sulfidic raw material with a high copper content, which raw material can be fed for example to a flash smelting furnace, to a furnace producing blister copper or to hydrometallurgic processes. As another product from the method according to the invention, there is obtained for instance a nickel bearing sulfate solution that can be treated as such, or precipitated as sulfide, hydroxide or a corresponding salt, which can then be fed in existing nickel production processes.

Various different leaching alternatives can be applied in the method according to the invention: the leaching can be based for example on sulfate leaching, chloride leaching or a combination of these. If the solution contains larger amounts of chloride for example, then the copper sulfide product (Cu_xS) obtained from the process is washed after filtering under cathodic potential, created either electrically or by chemicals, in case the product rich in Cu_xS is going to smelting. The same applies to other such products of the method of the present invention that are fed to other pyrometallurgical processes. Another preferred embodiment of the invention is one where leaching residue bearing precious metals is conducted to the production of nickel. In that case the nickel contained in the recirculation solution of a nickel process is subjected to conversion by iron sulfide, such as Fe_{1-x}S or FeS , according to the following reaction (1):



The obtained nickel sulfide can in that case be poor with respect to platinum and palladium, or it may contain a leaching residue that is rich in platinum, palladium and gold. When in this method both nickel and cobalt are mainly contained in the solution, cobalt can be separated from nickel when so desired, for example by liquid-liquid extraction or by precipitating the cobalt selectively by ozone as the compound CoOOH .

The invention is described in more detail below with reference to the appended drawing, Fig.1 being a flow diagram illustrating a preferred embodiment of the invention.

According to the figure, part of the ore or concentrate 1 based on copper sulfide and containing nickel and precious metals is conducted to leaching 2, where also is fed oxygen bearing gas 3 and sulfuric acid 4 as part of the feed of the method according to the invention. Part of the feed of the method according to the invention is conducted to a conversion step 5 following the leaching step 2.

Advantageously the material 9 fed in the conversion step 5 is the same ore or concentrate 1 that is fed in the leaching step 2. To the leaching step 2, there also is conducted at least part of the sulfate solution 6 obtained from the conversion step 5 and containing nickel.

5

In the leaching step 2, the copper sulfide based ore or concentrate 1 containing nickel and precious metals is leached and neutralized, so that in the leaching 2, the iron is obtained in the precipitate 7. The solution 8 obtained from the leaching 2 is conducted, together with the part that was not dissolved, to the
10 conversion step 5, where the copper is returned to sulfide form containing the precious metals by means of sulfide material 9 fed in the conversion step 5. The copper sulfide 10 containing the precious metals is removed from the conversion step 5 and conducted to be processed further. Part of the sulfate solution 6 from the conversion step 5 is returned back to the leaching step 2,
15 whereas part of the sulfate solution 6 is advantageously conducted for instance to a new conversion step 11, where iron sulfide 12 is fed for turning the nickel and possibly the cobalt to a sulfide containing product 13 that can be processed further, for example in order to produce pure nickel. The solution obtained from the conversion step 11 is combined with the solution 6 obtained from the
20 conversion step 5 and returned to leaching 2.

Example

A method according to the invention was applied for copper-nickel sulfide ore
25 that contained as concentrate 14.7 % by weight copper, 2.6 % by weight nickel, 30.5 % by weight sulfur and 138 ppm palladium and 39 ppm platinum. A total amount of 230 t concentrate was fed to the leaching step. The leaching was carried out as atmospheric leaching at the temperature of 80° C. From the leaching step, there were obtained 95 t solids going to the conversion step, as
30 well as a solution having a copper content of 32 t and a nickel content of 6 t. A quantity of 16 t chalcopyrite concentrate (CuFeS_2) was fed to the conversion step for turning the copper into sulfide form. By means of conversion, there was

obtained 50 t Cu_xS concentrate that contained precious metals, 9 kg platinum and 32 kg palladium, as well as 0.1 t nickel. The rest of the nickel was contained in the solution that was partly returned to the leaching step and partly conducted to nickel recovery in a new conversion step. Thus the ore that
5 originally contained a lot of nickel in sulfide form was concentrated to a concentrate containing a lot of copper, which concentrate can be used as feed in the further refining of copper.

CLAIMS

1. A method for processing sulfide ores containing precious metals, such as copper ores containing nickel, **characterized** in that the ore or concentrate (1) containing the precious metals is leached (2), and the iron contained in the solution is neutralized in oxidizing conditions by means of a ferrous recirculation solution (6) recirculated to the leach, and that the solution (8) from the leaching step and at least part of the solution residue is conducted to a conversion step (5), where iron bearing sulfide (9) is fed for turning the copper contained in the conversion step to copper sulfide concentrate (10) containing the precious metals, and that the solution (6) obtained from the conversion step is partly recirculated to the preceding leaching step (2) and partly conducted to the further treatment (11) of the components contained in the solution.
2. A method according to claim 1, **characterized** in that a sulfate based solvent is used in the leaching (2).
3. A method according to claim 1, **characterized** in that a chloride based solvent is used in the leaching (2).
4. A method according to claim 1, **characterized** in that a combination of a sulfate based and chloride based solvent is used in the leaching (2).
5. A method according to any of the preceding claims, **characterized** in that the leaching (2) is carried out as atmospheric leaching at the temperature of 50 – 105° C.
6. A method according to any of the preceding claims 1 – 4, **characterized** in that the leaching (2) is carried out as autoclave leaching.
7. A method according to any of the preceding claims, **characterized** in that the conversion step (5) is carried out at the temperature of 90 – 200° C.

8. A method according to claim 7, **characterized** in that the conversion step (5) is carried out at the temperature of 150 – 190° C.
- 5 9. A method according to any of the preceding claims, **characterized** in that part of the solution (6) obtained from the conversion step (5) is conducted to at least one further conversion step (11) for turning the components contained in the solution into sulfidic form in the presence of an iron bearing sulfide.
- 10 10. A method according to any of the preceding claims, **characterized** in that part of the solution (6) obtained from the conversion step (5) is conducted to a new further conversion step that is carried out for sulfidizing nickel.
11. A method according to any of the preceding claims 1 – 9, **characterized** in
15 that part of the solution obtained from the conversion step (5) is conducted to a new further conversion step that is carried out for sulfidizing cobalt.
12. A method according to any of the preceding claims, **characterized** in that the sulfide material used in the conversion (5) is the same material as the
20 material going to leaching.
13. A method according to any of the preceding claims 1 – 11, **characterized** in that the sulfide material used in the conversion (5) is a different material than the material going to leaching.
- 25 14. A method according to any of the preceding claims, **characterized** in that at least part of the precious metal containing leaching residue (13) of the leaching step is conducted to a further conversion step that is carried out for sulfidizing nickel.

15. A method according to any of the preceding claims, **characterized** in that the leaching step (2) and the conversion step (5) are controlled at least partly by means of mineral-specific potentials, impedance values or content values.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 2004/000452

A. CLASSIFICATION OF SUBJECT MATTER

IPC7: C22B 3/06 // C22B 15:00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: C22B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-INTERNAL, WPI DATA, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4256553 A (FRANK A. BACZEK ET AL), 17 March 1981 (17.03.1981), column 5, line 3 - line 6; column 5, line 49 - line 52, figure 1, abstract --	1-15
A	US 6319389 B1 (GEARLD F. FOUNTAIN ET AL), 20 November 2001 (20.11.2001), column 11, line 16 - line 22, abstract --	1-15
A	US 5902474 A (DAVID L. JONES), 11 May 1999 (11.05.1999), abstract --	1-15

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

17 November 2004

Date of mailing of the international search report

19 -11- 2004

Name and mailing address of the ISA/
Swedish Patent Office
Box 5055, S-102 42 STOCKHOLM
Facsimile No. +46 8 666 02 86

Authorized officer

Mårten Hulthén/MP
Telephone No. +46 8 782 25 00

INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 2004/000452

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 3957602 A (ROBERT K. JOHNSON ET AL), 18 May 1976 (18.05.1976), abstract --	1-15
A	US 3891522 A (DONALD R. MCKAY ET AL), 24 June 1975 (24.06.1975); column 9, line 21 - line 26, abstract --	1-15
A	US 4049770 A (GODEFRIDUS MARIA SWINKELS ET AL), 20 Sept 1977 (20.09.1977), abstract --	1-15
A	US 2755172 A (PATRICK J. MCGAULEY ET AL), 17 July 1956 (17.07.1956), column 1, line 16 - line 20; column 2, line 24 - line 28 --	1-15
A	US 5108495 A (SEPPO O. HEIMALA ET AL), 28 April 1992 (28.04.1992), abstract -- -----	1-15

INTERNATIONAL SEARCH REPORT

Information on patent family members

30/10/2004

International application No.

PCT/FI 2004/000452

US	4256553	A	17/03/1981	CA	1156050	A	01/11/1983

US	6319389	B1	20/11/2001	AU	7173100	A	31/05/2001
				CA	2326081	A	24/05/2001
				ZA	200006842	A	05/06/2001

INTERNATIONAL SEARCH REPORT

Information on patent family members

30/10/2004

International application No.

PCT/FI 2004/000452

US	5902474	A	11/05/1999	AU	694960 B,C	06/08/1998
				AU	708844 B	12/08/1999
				AU	709602 B	02/09/1999
				AU	4296096 A	30/12/1996
				AU	4476696 A	30/12/1996
				AU	5888996 A	30/12/1996
				BG	62178 B	30/04/1999
				BG	62180 B	30/04/1999
				BG	62290 B	30/07/1999
				BG	102132 A	31/07/1998
				BG	102133 A	31/07/1998
				BG	102149 A	31/08/1998
				BR	9608483 A	06/07/1999
				BR	9608499 A	06/07/1999
				BR	9608624 A	29/06/1999
				CA	2221781 A	19/12/1996
				CA	2221930 A	19/12/1996
				CA	2221940 A,C	19/12/1996
				CA	2356048 A,C	19/12/1996
				CA	2356050 A,C	19/12/1996
				CN	1052265 B	10/05/2000
				CN	1055971 B	30/08/2000
				CN	1057344 B	11/10/2000
				CN	1186523 A	01/07/1998
				CN	1186524 A	01/07/1998
				CN	1187220 A	08/07/1998
				DE	69606036 D,T	08/06/2000
				DE	69610208 D,T	26/04/2001
				DE	69612617 D,T	18/04/2002
				DE	69626048 D	00/00/0000
				DE	69629845 D,T	08/07/2004
				DK	832302 T	20/11/2000
				DK	832306 T	08/05/2000
				DK	930373 T	13/10/2003
				EP	0832302 A,B	01/04/1998
				SE	0832302 T3	
				EP	0832303 A,B	01/04/1998
				EP	0832306 A,B	01/04/1998
				SE	0832306 T3	
				EP	0924307 A,B	23/06/1999
				EP	0930373 A,B	21/07/1999
				ES	2144240 T	01/06/2000
				ES	2153950 T	16/03/2001
				ES	2159351 T	01/10/2001
				FI	974427 A	05/12/1997
				FI	974428 A	05/12/1997
				JP	11506166 T	02/06/1999
				JP	11506167 T	02/06/1999
				JP	11510559 T	14/09/1999
				NO	975707 A	05/12/1997
				OA	10643 A	24/09/2002
				PL	323593 A	14/04/1998
				PL	323782 A	27/04/1998
				PL	323799 A	27/04/1998
				RU	2174562 C	10/10/2001

INTERNATIONAL SEARCH REPORT

Information on patent family members

30/10/2004

International application No.

PCT/FI 2004/000452

US	5902474	A	11/05/1999	RU	2178007	C	10/01/2002
				RU	2179192	C	10/02/2002
				TR	9701568	T	00/00/0000
				TR	9701569	T	00/00/0000
				TR	9701570	T	00/00/0000
				TR	9802185	T	00/00/0000
				TR	9802186	T	00/00/0000
				TW	408186	B	00/00/0000
				TW	493008	B	00/00/0000
				US	RE37251	E	03/07/2001
				US	5650057	A	22/07/1997
				US	5855858	A	05/01/1999
				US	5869012	A	09/02/1999
				US	5874055	A	23/02/1999
				US	6054105	A	25/04/2000
				US	6383460	B	07/05/2002
				US	20020012621	A	31/01/2002
				WO	9641026	A	19/12/1996
				WO	9641027	A	19/12/1996
				WO	9641029	A	19/12/1996
				ZA	9604866	A	07/01/1997
				US	5645708	A	08/07/1997
				EP	0804624	A,B	05/11/1997
				SE	0804624	T3	
				US	5431788	A	11/07/1995
				WO	9619593	A	27/06/1996

US	3957602	A	18/05/1976	NONE
----	---------	---	------------	------

US	3891522	A	24/06/1975	NONE
----	---------	---	------------	------

US	4049770	A	20/09/1977	US	3964901	A	22/06/1976
----	---------	---	------------	----	---------	---	------------

US	2755172	A	17/07/1956	US	2662009	A	08/12/1953
----	---------	---	------------	----	---------	---	------------

US	5108495	A	28/04/1992	AU	615295	B	26/09/1991
				AU	3456289	A	16/11/1989
				CA	1337742	A,C	19/12/1995
				FI	82773	B,C	31/12/1990
				FI	882261	A	14/11/1989
				MX	170755	B	13/09/1993
